

Effects of Protonation on Homogeneous Electron Transfer Reaction in the Solid-State

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Mechanically attached solid state films of $[\text{Os}(\text{DMObpy})_3]\text{PF}_6$ have been formed on platinum microelectrodes. Scanning electron microscopy reveals that mechanical attachment of the microcrystalline solid to electrode surfaces leads to the formation of an array of microscopically small sites. At high scan rates ($50 < \nu < 500 \text{ mVs}^{-1}$), a reversible diffusion-controlled voltammetric response is obtained for these films. Upon repeated electrochemical cycling in 0.1 M perchloric acid, the film becomes more homogeneous and reveals evidence of nucleation and crystal growth. The pH of the electrolyte is found to have profound effects on the formal potential of the $\text{Os}^{2+/3+}$ redox reaction. As the pH of the contacting electrolyte is systematically adjusted from pH 7.0 to 1.0, the formal potential shifts cathodically from 0.727V to 0.250V. Under steady state and semiinfinite conditions (slow and fast scan rate), it is possible to determine the fixed site concentration and apparent diffusion coefficients of the compound. A comparison between the heterogeneous rate constants for solution and solid phase has also been examined.